Final Report for AOARD Grant 09-4050

"Functionalizing Carbon Nanotubes and Related Nanostructures for Various Applications"

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Abstract:

Development in carbon nanotubes (CNTs), silicon nanotips (SiNTs) and related hybrids has been demonstrated in various applications, such as photovoltaic, optoelectronics, sensing and energy. Specifically, four cases are highlighted here: (1) single-walled CNTs dispersed in polymer matrix for photovoltaic, (2) ZnO coated SiNTs for light-emitting optoelectronic, (3) hybrid ZnO nanorods/Cu nanoparticles as catalyst for microreformers with high conversion efficiency, and (4) composite polyaniline nanowires/carbon cloth as flexible supercapacitor with high gravimetric and area-normalized capacitance.

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14. ABSTRACT **This is a report on the use of carbon nanotubes, silicon nanotips, and related hybrids in various applications, such as photovoltaics, optoelectronics, sensing, and energy.**						
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Introduction

Over the last few years, my group has established a strong program on various low-dimensional nanomaterials, such as carbon nanotubes (CNTs), Si nanotips (SiNTs), GaN nanowires, and related advanced nano-composites. Building on these ground works, a number of photovoltaic, optoelectronic, sensing and energy/power devices that utilize the above-mentioned nanomaterials as their key components have been developed. Nano-structured system with well-controlled interfaces that either giving better catalytic activity and subsequent current carrier conduction or blending electro-/photo-active donor and acceptor plays a decisive role in fabricating high-efficiency electrochemical, optoelectronic or photovoltaic devices. Our main emphases have been placed on (i) studying the energetic and formation kinetics of the nanostructures and their composites; (ii) functionalizing the surface of these nanostructures and their interface properties; (iii) analyzing the interface/surface structure and physical/chemical property in nanoscale; (iv) designing "smart" micro-devices with interface-controlled properties. As will be exemplified below, novel designs using the inherently high surface area and large aspect ratio of these nanostructures have shown unique properties and device performance unmatched by their bulk counterparts.

Categorized Summary of Research Outcomes

(1) Single-walled CNTs Dispersed in Polymer Matrix for Photovoltaic

Solvent effects on the dispersion of the single-walled CNTs in the poly(3-hexylthiophene) (P3HT) matrix were investigated. Bulk heterojunctions of P3HT and CNTs have been fabricated and their photovoltaic performance has been studied. Not only the morphology of P3HT but also the CNTs dispersion in P3HT matrix show strong dependence on the solvents. Atomic force microscopy images suggest that P3HT forms poor crystal structure in chloroform but better in solvents that have relatively high boiling points such as chlorobenzene, toluene, and *o*-xylene (Figure 1). However, the results of quench rate of photoluminescence and the exciton lifetime decay rate in CNT/P3HT indicate that a good SWNT dispersion can only be obtained in chloroform and chlorobenzene cases. This suggests that more effective interfaces can be formed when these two solvents are used and thus leads to enhanced charge separation rate, which eventually will benefit photovoltaic performance. Our photovoltaic demonstration further confirms the idea and suggests that using chlorobenzene for preparation of SWNT/P3HT photovoltaic devices will give more promising results.

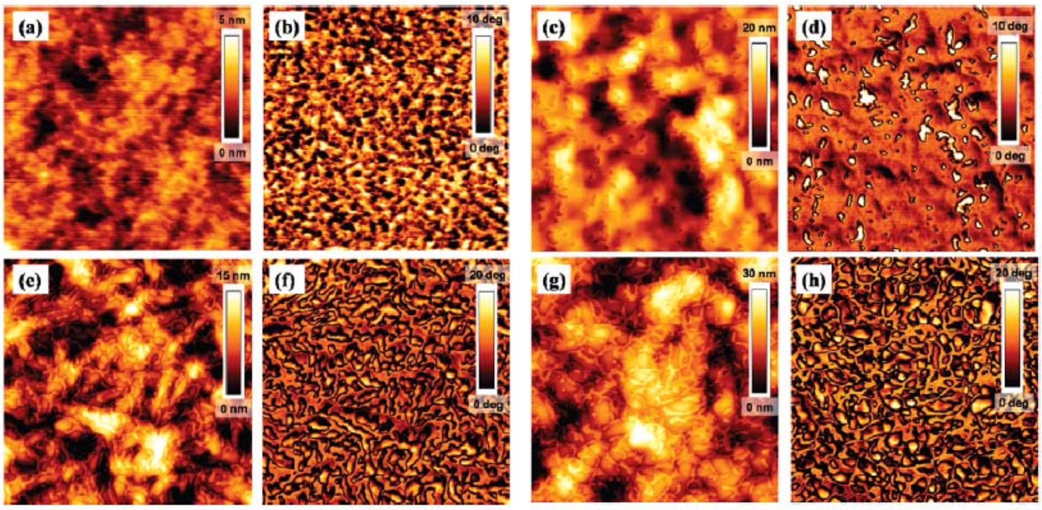

Figure 1 AFM topography and phase contrast images of pristine P3HT films spin-coated from different solvents: (a) (b) CF, (c) (d) CB, (e) (f) o-xylene, and (g) (h) toluene. The morphology image is on the left side and phase one is on the right for each solvent. The image size is 1 by 1 μm with resolution of 512 X 512 pixels.

(2) ZnO Coated SiNTs for Light-emitting Optoelectronics

Here, we demonstrate a new and general approach to generating sufficient carrier injection and efficient light emission from a Si nanotip array. As illustrated schematically in Figure 2, an *n*-type ZnO layer was grown by pulsed laser deposition (PLD) onto the *p*-type SiNTs to form *p*-*n* heterojunctions.

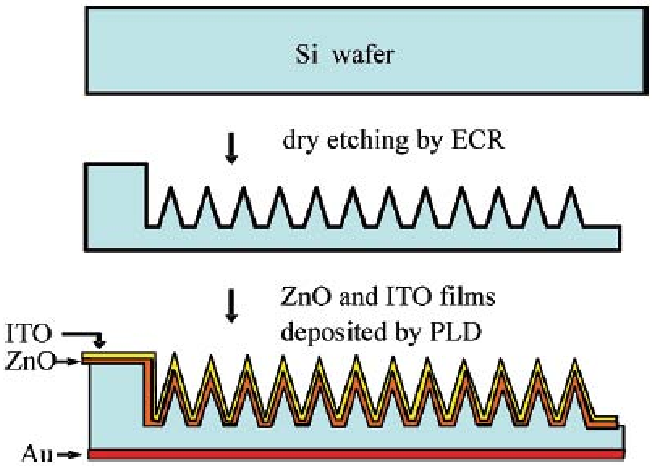

Figure 2 Schematic diagrams showing the fabrication technique of our ZnO/SiNTs arrayed light-emitting-diodes.

We further show that the unique geometry of the nanotip gives enhanced effective field, thus enables us to operate the arrayed light-emitting-diodes (LED) with a very low voltage (~2.4 V), unmatched by their planar film counterparts. Our new approach for fabricating an efficient, large-area silicon-based nanotip LED array could pave the way for integrating Si ultralarge-scale integrated circuits with electro-optics to overcome the speed limitation of electrical interconnects and to add extra functionalities on silicon chips.

(3) Hybrid ZnO Nanorods/Cu Nanoparticles as Catalyst for Microreformers

The idea of using microreformers is highly attractive for several applications, such as on-board hydrogen sources for small vehicles and portable fuel cells. However, two key issues have hindered the realization of microreformers for catalysis, namely, poor adhesion between the catalyst layer and the microchannels and poor utilization of catalyst layer deposited in the form of thick film. Notwithstanding, several approaches investigated to overcome these issues, catalyst immobilization, and its efficient utilization inside the microchannel remains a challenge. Most of these approaches involve a two-step process, wherein active catalysts are prepared in the first step, followed by its immobilization on the surface of the microchannels in the second step. Herein, we report a simple and reliable method for integrating in-situ synthesis of catalyst and its immobilization for microreformer applications (Figure 3).

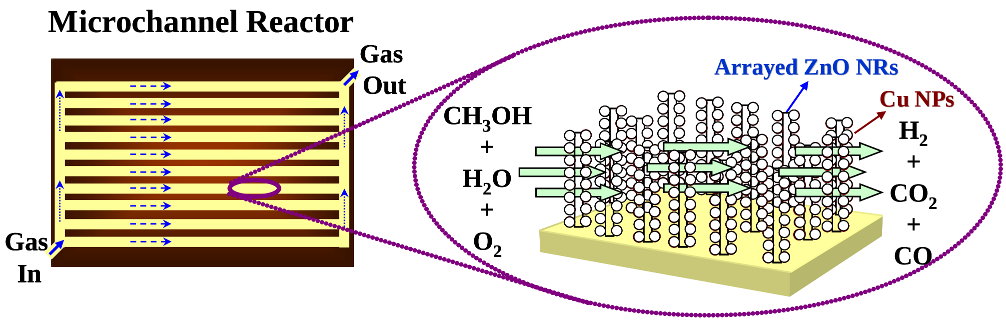

Figure 3 Schematic illustration of an in-situ synthesis of Cu nanocatalysts and arrayed ZnO nanorods supports.

The ZnO nanorods (NR) arrays were first grown on a microchannel reactor using a simple template-free aqueous approach. A simple mixture of copper salts, aqueous media, and ZnO NR arrays at low temperature subsequently resulted in spontaneous formation of cable-like nanostructures. As the ZnO NR@Cu NP nanocomposites were synthesized in-situ directly on the microreactor, the arrayed ZnO@Cu nanocomposites were strongly anchored onto the microchannel. The strong mechanical anchorage of nanostructured catalysts on the surface of microchannel was shown by the observation that no material loss occurred after sonication in the water for several hours. The methanol conversion behavior (Figure 4) and the interaction between Cu NPs and ZnO NRs were studied by several analytical techniques, including X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, and temperature-programmed reduction. The methanol conversion rate over the arrayed ZnO@Cu is as high as 93%, with a hydrogen production rate of 183 mmol/h per gram catalyst at 250°C. Both rates are significantly higher than those obtainable with the commercial catalysts. Surprisingly, a CO concentration of only 170–210 ppm was detected during these runs at 250°C, much lower than circa 1000 ppm for the commercial catalysts.

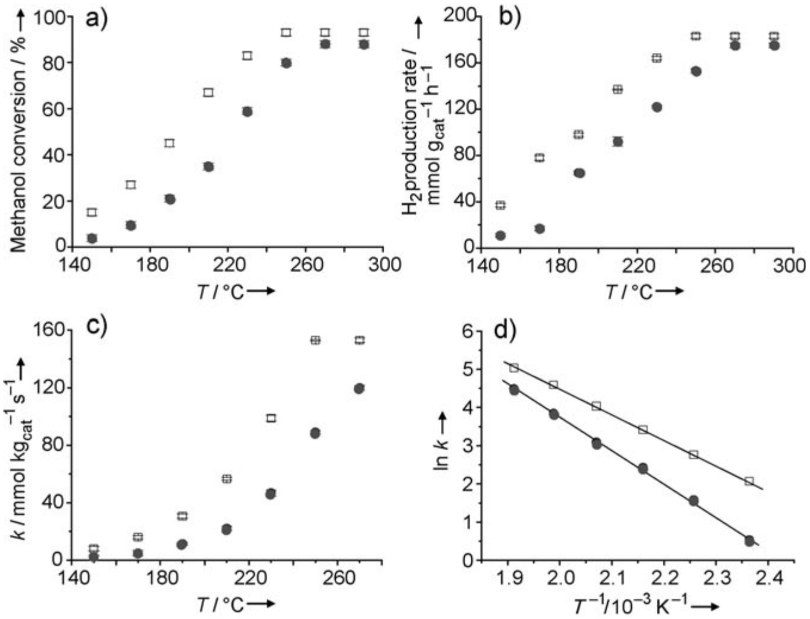

Figure 4 Comparative studies of the methonal conversion behaviors as a function of temperature for the ZnO NR@Cu NP nanocomposites (open symbols) and commercial catalysts (solid symbols).

(4) Flexible Supercapacitor Based on Polyaniline Nanowires/Carbon Cloth with both High Gravimetric and Area-normalized Capacitance

We present a simple and convenient route to directly fabricate polyaniline nanowires (PANI-NWs) onto the surface of carbon cloth (CC) by an electrochemical method. CC was specifically selected as the current collector due to its cost-effectiveness, high conductivity, reasonable chemical stability, and a 3D structure with high porosity (hence high surface area) for PANI-NWs growth. In addition, the flexible nature of CC is also preferable for fabrication of flexible-electrode from the design and packaging perspectives. Moreover, unlike other powdered-type supercapacitors, the PANI-NWs/CC is a binder-free electrode that enables reduction in interfacial resistance and enhances the electrochemical reaction rate. As regards to the porosity of PANI-NWs/CC, the network of comparatively large pore sizes in CC are expected to facilitate the diffusion of electrolyte into the electrode material, thus providing channels for rapid transport of conductive ions. As shown in Figure 5, an excellent capacitive performance of this novel PANI-NWs/CC electrode, that simultaneously exhibits high gravimetric as well as area-normalized capacitance values, is demonstrated.

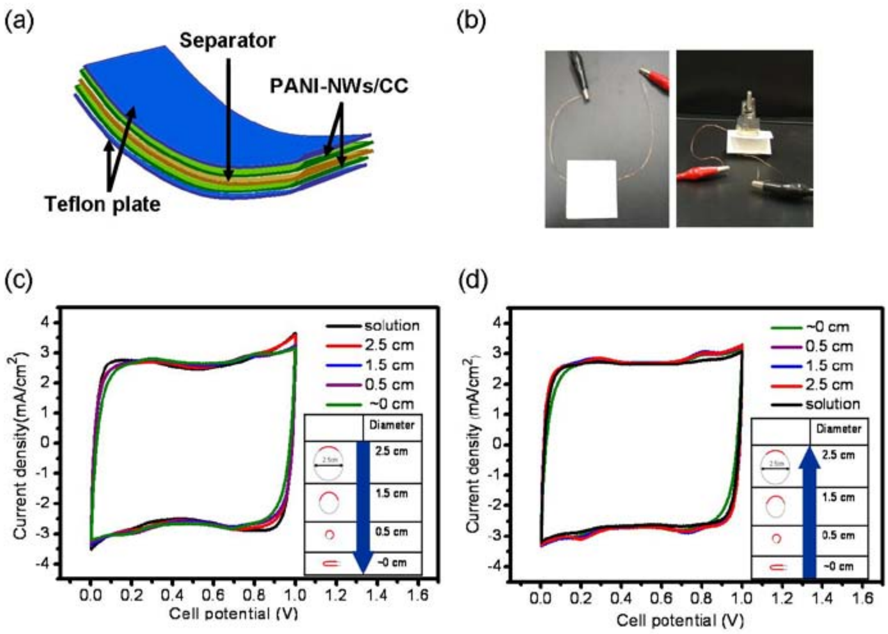

Figure 5 (a) Schematic of the flexible supercapacitor made of PANI-NWs/CC, using a conventional two-electrode system, (b) Mechanical flexibility of PANI capacitors, for flat sheet (left), and curvature cells (right). Cyclic voltammograms: (c) PANI capacitor bended with diameters of curvatures from 2.5 to 0 cm (d) PANI capacitor returned the diameters from 0 to 2.5 cm at a scan rate of 10 mVs^{-1}.

List of Publications: Please list any publications, conference presentations, or patents that resulted from this work.

I. Selective Project-related Publications

Overall, 32 papers were published during this project period of time. Financial support from the AFOSR/AOARD has been indicated explicitly in the following 8 papers.

(1) 'Nanostructured ZnO Nanorod@Cu Nanoparticle as Catalyst for Microreformers', Yan-Gu Lin, Yu-Kuei Hsu, San-Yuan Chen, Yu-Kai Lin, Li-Chyong Chen* and Kuei-Hsien Chen*, *Angew. Chem. Int. Ed. 48*, 7586 (2009).

(2) 'Efficient Hydrogen Production using Cu-based Catalysts Prepared via Homogeneous Precipitation', Yu-Kai Lin, Yi-Han Su, Yun-Hsin Huang, Chia-Jung Hsu, Yu-Kuei Hsu, Yan-Gu Lin, Ko-Hsiung Huang, San-Yuan Chen, Kuei-Hsien Chen* and Li-Chyong Chen*, *J. Mater. Chem.19*, 9186 (2009).

(3) 'Molecule-modulated Photoconductivity and Gain-amplified Selective Gas Sensing in Polar GaN Nanowires', Reui-San Chen, Kuei-Hsien Chen, Chien-Yao Lu and Li-Chyong Chen*, *Appl. Phys. Lett. 95*, 233119 (2009).

(4) 'Room-temperature Negative Photoconductivity in Degenerate InN Thin Films with a Supergap Excitation', Pai-Chun Wei, Surojit Chattopadhyay*, Min-De Yang, Shih-Chang Tong, Ji-Lin Shen, Chien-Yao Lu, Han-Chang Shih, Li-Chyong Chen, and Kuei-Hsien Chen*, *Phys. Rev. B 81*, 045306 (2010).

(5) 'Heteroepitaxy of *m*-plane ($10\underline{1}0$) InN on (100)-γ-$LiAlO_2$ Substrates and its Strong Anisotropic Optical Behaviors', Ching-Lien Hsiao*, Jr-Tai Chen, Hsu-Cheng Hsu, Ying-Chieh Liao, Po-Han Tseng, Yen-Ting Chen, Zhe-Chuan Feng, Li-Wei Tu, Mitch M. C. Chou, Li-Chyong Chen*, and Kuei-Hsien Chen*, *J. Appl. Phys. 107*, 073502 (2010).

(6) 'Influence of Solvent on the Dispersion of Single-walled Carbon Nanotubes in Polymer Matrix and their Photovoltaic Performances', Cheng-Kai Chang, Jeong-Yuan Hwang, Wei-Jung Lai, Wei-Ting Yie, Chun-Wei Chen, Ching-I Huang, Kuei-Hsien Chen* and Li-Chyong Chen*, *J. Phys. Chem. C 114*, 10932 (2010).

(7) 'Flexible Supercapacitor Based on Polyaniline Nanowires/Carbon Cloth with both High Gravimetric and Area-normalized Capacitance', Ying-Ying Horng, Yi-Chen Lu, Yu-Kuei Hsu, Chia-Chun Chen, Li-Chyong Chen* and Kuei-Hsien Chen*, *J. Power Sources 195*, 4418 (2010).

(8) 'Anti-reflecting and Photonic Nanostructures', S. Chattopadhyay*, Y. F. Huang, Y. J. Jen, A. Ganguly, K. H. Chen and L. C. Chen*, an invited review article in A. G. Cullis and S. S. Lau, Eds., *Materials Science and Engineering Review 69*, pp. 1-35, Elsevier, 2010.

II. Selective Project-related Invited Talks at International Conferences

[AFOSR/AOARD has been indicated explicitly in the following presentations.]

(1) 216th Meeting of the Electrochemical Society (October 4-9, 2009), Symposium

E6: One-dimensional Nanoscale Electronics and Photonic Devices 3, **Keynote Speaker**, on "*Multifunctional Si nanotips-array: antireflection and tip-enhanced electroluminescence and magneto-resistance*", Vienna, Austria

(2) The Third International Conference on One-dimensional Nanomaterials, ICON 2009 (December 7-9, 2009), on *"Si nanotips and related hetero-junction arrays: from antireflection to tip-enhanced luminescence and magneto-resistance"*, Atlanta, GA, USA

(3) International Conference on Nanoscience and Nanotechnology, ICONN 2010 (February 24-26, 2010), **Plenary Speaker**, on "*Si nanotips and related hetero-junction arrays: from antireflection to tip-enhanced luminescence and magneto-resistance*", Kattankulathur, Tamil Nadu, India

(4) CIMTEC-5th Forum on New Materials (June 13-18, 2010), Symposium FJ: Materials and Technologies for Solid State Lighting, on "*Heteroepitaxial growth of m-plane InN on* $LiAlO_2$ *substrates and its strong anisotropic optical behaviors*", Montecatini Terme, Tuscany, Italy

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